scribed. Attempts to prepare suitable compounds of type (VII) (compare Ring Index No. 2264) have been commenced. We shall follow the subsequent work of Buhle, Moore and Wiselogle in this field with interest.

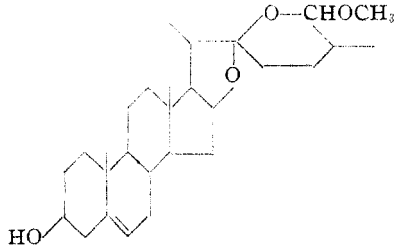
THE UNIVERSITY OF MELBOURNE H. H. HATT
MELBOURNE, AUSTRALIA EMILY F. H. STEPHENSON

RECEIVED APRIL 28, 1943

SAPONINS AND SAPOGENINS. XXIII. THE CONSTITUTION OF BETHOGENIN[1]

Sir:

We should like to propose the following structural formula for bethogenin.[2,3]



This proposal is based on the results previously reported and on new data which follow.

Reaction of bethogenin or its acetate with hydrogen bromide in acetic acid eliminates methoxyl and gives a diacetate, $C_{31}H_{46}O_6$, m. p. 148–149°, $[\alpha]^{26}D$ − 161° in dioxane, which forms a dioxime, $C_{31}H_{48}O_6N_2$, m. p. 194–195°. Reduction of the hydrogen bromide reaction product with hydrogen and Adams platinum catalyst in alcoholic solution gives a dihydrodiacetate, $C_{31}H_{48}O_6$, m. p. 116–117°, $[\alpha]^{22}D$ −11° in dioxane. The ultraviolet absorption spectrum of this compound indicates that carbonyl still is present but a test with tetranitromethane for the double bond indicates that it has been reduced.

Reaction of bethogenin with hydroxylamine in pyridine gives a dioxime[2] $C_{27}H_{44}O_4N_2$, which no longer contains methoxyl.

Several products of catalytic hydrogenation of bethogenin have been isolated. The absorption of one mole of hydrogen in the presence of platinum in alcoholic solution removes methoxyl to give a product which contains both a double bond and a carbonyl group and which forms a diacetate, $C_{31}H_{46}O_6$, m. p. 142–144°, $[\alpha]^{24}D$ −156° in dioxane. Exhaustive catalytic reduction of bethogenin in alcoholic solution gives $C_{27}H_{46}O_4$, m. p. 203–208.6°, $[\alpha]^{25}D$ −57.7° in dioxane. This product no longer contains a double bond or a carbonyl group. On reaction with acetic anhydride in pyridine it loses one molecule of water and forms a monoacetate, $C_{29}H_{46}O_4$, m. p. 204–207.5°, $[\alpha]^{25}D$ −62.2° in dioxane. On mixing with tigogenin acetate, m. p. 204–207.5°, $[\alpha]^{22.5}D$ −64.0° in dioxane, no depression in melting pont was observed.

We hope to be able to publish shortly the details of the above experiments and an interpretation of the reactions involved.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY C. R. NOLLER
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RECEIVED JULY 26, 1943

THE BOROHYDRIDES OF GALLIUM

Sir:

At the present time the borohydrides of three metals are known: lithium borohydride,[1] $LiBH_4$; methylberyllium borohydride,[2] CH_3BeBH_4; beryllium diborohydride,[2] $Be(BH_4)_2$; and aluminum triborohydride,[3] $Al(BH_4)_3$. These compounds are of considerable interest because of their unusual chemical and physical properties. The aluminum and beryllium compounds are of particular interest because they are the most volatile derivatives of these metals known. It therefore seems desirable to extend the study of the borohydrides to other metals. In the present communication we wish to report preliminary observations on the borohydrides of gallium.

In a typical experiment, trimethylgallium was treated with an excess of diborane at room temperature. A small decrease in pressure was observed over a period of three hours. At the end of this time a metallic film suddenly appeared on the walls of the reaction vessel, accompanied by a rapid increase in the pressure, and the formation of non-condensable gas (hydrogen). The film was

(1) This Communication was submitted prior to the publication of the Communication by Marker and co-workers (THIS JOURNAL, **65**, 1658 (1943)) in which a similar formula for bethogenin was proposed. The published reactions of bethogenin and kryptogenin are explainable by either formulation. On the basis of the formula for bethogenin proposed by us, kryptogenin would be a ketoaldehyde rather than a diketone. Preliminary tests by one of us (D. F.) indicate that this actually is the case. The product of the action of hydrogen bromide in glacial acetic acid on bethogenin is colored pink by Schiff reagent and gives a red color with 1,4-dihydroxynaphthalene in glacial acetic acid and hydrochloric acid [Raudnitz and Puluj, *Ber.*, **64**, 2212 (1931)] while diosgenin and the diketo-compounds tigogenoic acid, chlorogenoic acid, and methyl chlorogenoate diacetate all give negative results with these reagents—C. R. NOLLER, M. R. BARUSCH and DAVID FRAZIER (August 16, 1943).

(2) Lieberman, Chang, Barusch and Noller, THIS JOURNAL, **64**, 258 (1942).

(3) Noller and Barusch, *ibid.*, **65**, 1435 (1943).

(1) Schlesinger and Brown, THIS JOURNAL, **62**, 3429 (1940).

(2) Burg and Schlesinger, *ibid.*, **62**, 3425 (1940).

(3) Schlesinger, Sanderson and Burg, *ibid.*, **62**, 3421 (1940).

identified as gallium by its melting point (30°) and by conversion into gallium trichloride (m. p. 75°). For each mole of trimethylgallium taken, 3.1 moles of methylated diboranes (calculated as monomethyldiborane), 1.53 moles of hydrogen, and 1.02 moles of gallium were obtained. The over-all reaction can thus be represented by the equation

$$Ga(CH_3)_3 + 3B_2H_6 = Ga + 3CH_3B_2H_5 + 3/2H_2$$

In other experiments the appearance of the film and the formation of hydrogen was not observed over a period of time as long as twenty-four hours. It seems probable that gallium borohydride is first formed in the course of the reaction but it then undergoes a rapid autocatalytic decomposition. The equations for these reactions may be written as

$$2(CH_3)_3Ga + 9B_2H_6 = 2Ga(BH_4)_3 + 6CH_3B_2H_5$$

and

$$2Ga(BH_4)_3 = 2Ga + 3B_2H_6 + 3H_2$$

The reaction between trimethylgallium and diborane at −45° resulted in the formation of practically pure dimethylgallium borohydride. Trimethylgallium, 13.1 cc., was treated with several portions of diborane until no further reaction was apparent. The quantity of diborane reacting was 18.7 cc.; monomethyldiborane, 12.2 cc., was obtained. These data lead to the empirical formula $(CH_3)_{2.06}GaB_{0.99}H_{3.91}$, for the product. The homogeneity of the product was demonstrated by fractionation into several parts, all of which showed the same vapor tension. The product thus obtained is a volatile crystalline solid which melts into a clear colorless liquid at +1.5°. It is stable at −80° but undergoes slow decomposition at room temperature. The vapor density confirms the monomeric formula (molecular weight found, 115; calculated, 114.5). It can be concluded that the reaction between diborane and trimethylgallium proceeds according to the equation

$$2(CH_3)_3Ga + 3B_2H_6 = 2(CH_3)_2GaBH_4 + 2CH_3B_2H_5$$

The new compound exhibits a vapor tension of 14 mm. at 0° and 51 mm. at 24°; the extrapolated boiling point is 92°; Trouton's constant is 23.5 cal./mole-deg.

The reactions of dimethylgallium borohydride are being studied in detail, and the volatile intermediates in the room temperature reaction between diborane and trimethylgallium are being further investigated.

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GEORGE W. SCHAEFFER

RECEIVED AUGUST 11, 1943

NEW BOOKS

Chemistry and Methods of Enzymes. By JAMES B. SUMNER, Professor of Biochemistry, and G. FRED SOMERS, Instructor in Biochemistry, Cornell University. Academic Press, Inc., Publishers, 125 East 23rd Street, New York, N. Y., 1943. xi + 365 pp. 15.5 × 23.5 cm. Price, $5.00.

Here, surprisingly enough, is the first work in the English language which presents a general survey of all classes of enzymes. Several works have appeared heretofore dealing with either the oxidative or the proteolytic enzymes but none has attempted to cover the whole field. This present survey is not, however, an exhaustive one of the type to be found in the German literature. As the authors state in their preface, they have attempted to give the research worker and advanced student a general survey of enzyme chemistry without presenting too much detail on any one subject. They appear to have accomplished this aim in a highly satisfactory manner.

The book is divided into four parts. The first part consists of a chapter on the general properties of enzymes. Part two deals with the hydrolytic enzymes and contains six chapters with the following titles: Esterases, Carbohydrases, Enzymes of Carbohydrate Metabolism, Nucleases, Amidases, Proteolytic Enzymes. The third part is composed of nine chapters treating the oxidative enzymes. These chapters are entitled: Oxidizing Enzymes, The Iron Enzymes, The Copper Enzymes, Dehydrogenases Containing Coenzymes 1 and 2, Oxidases which Transfer Hydrogen to Cytochrome, The Yellow Enzymes, Nuclein Desaminases, Miscellaneous Oxidases, Desmolases. Part four consists of two chapters—one on hydrases and mutases, the other on carbohydrate metabolism. In all, some 165 enzymes are thus covered. In most cases, the history, occurrence, action, specificity, method of activity measurement, properties, and the method of preparation of the enzyme are outlined briefly. Ample references are given to the more important original articles in the literature.

Twenty-two of the enzymes discussed are listed as having been obtained in crystalline form. The methods for crystallization of some of these sound so simple that the novice could well gain the impression that one might well isolate and crystallize a new enzyme over the weekend. If he